

**Mandatory Greenhouse Gas Reporting for the
California Petroleum Refinery and
Exploration and Production Sectors:
Draft Regulation Concepts**

The Petroleum Refinery Sector

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Oil and Gas Exploration and Production (E & P) Sector

1. Who will report?
2. What GHGs will be reported?
3. What emission sources will be reported?

The Petroleum Refinery Sector

Background Information

- 1. Who will report?** – The 21 crude oil refineries in California are major sources of greenhouse gas emissions (GHGs) and would report their emissions on an annual basis.
- 2. What GHGs will be reported?** –All gases for which calculation methods are specified in ARB's regulation will be reported. Major GHG gas emissions from refinery operations are CO₂, CH₄, and N₂O. A simple mass balance calculation for HFCs will be included in the regulations and this method will be used by refineries where significant amounts of HFC refrigerants are used.
- 3. What emissions sources will be reported?**
 - a. Stationary Combustion - including combustion emissions from co-generation facilities.
 - b. Process emissions
 - i. Hydrogen plants¹
 - ii. Catalytic cracking
 - iii. Sulfur recovery
 - iv. Asphalt production
 - c. Fugitive emissions
 - i. Wastewater treatment
 - ii. Storage tanks
 - iii. Process emissions
 - iv. Flaring
- 4. Fuel specific emission factor** – In order to accurately determine GHG emissions from the petroleum refining sector, it is critical that the hydrocarbons used both as fuels and chemical feedstock be accurately characterized.
 - a. Refinery fuel gas

Refinery fuel gas (RFG) can comprise 50% or more of the fuel combusted in a typical refinery. RFG is derived from the crude oil distillation process and is used to fuel boilers, heaters, turbines, etc. RFG is also used as a chemical feedstock (hydrogen source) in some refinery hydrogen plants. Refinery fuel gas composition may vary significantly on relatively short

¹ Hydrogen Plants will be subject to GHG reporting whether or not they are located at or associated with refineries. A hydrogen plant may not fall under the operational control of the refinery where it is located. If this is the case, it will report as a separate entity.

time scales; thus HHV (High Heating Value) and CC (Carbon Content) determinations must be made at appropriate sampling locations and at sufficiently short time intervals to accurately determine GHG emissions from the combustion and consumption of this highly variable hydrocarbon mixture.

b. LPG

LPG (Liquefied Petroleum Gas) is also derived from the distillation of crude oil. LPG is also used as a fuel in the refining process. When single component fuels (e.g. propane) are combusted, literature HHV and emissions factors may be used. The HHV of fuel mixtures (e.g. butane and propane) must be determined daily.

c. Natural gas

The natural gas used in a refinery, both as a fuel and feedstock, is typically supplied by a third party. HHV must be determined weekly, and CC monthly, either by the supplier or the refiner.

d. Naphtha

Naphtha (a mixture of hydrocarbons) is derived from the crude distillation process and may be used as a feedstock for the production of hydrogen. This fraction is usually mixed with other gases such as NG and RFG when it is used to produce hydrogen. Daily composition data is required for this hydrocarbon mixture.

GHG Reporting Specifics

5. Stationary Combustion

a. Carbon dioxide

i. Non-standard fuels (RFG)

Both HHV and CC must be determined for non-standard fuels such as RFG and LPG. Given the highly variable nature of refinery derived fuels, using a literature derived emission factor can result in unacceptably large errors. Thus a fuel specific emission factor must be calculated and emission calculations performed on a frequent basis to insure accuracy.

ARB staff propose that emissions factors (mass CO₂/Btu) be calculated for RFG using HHV and CC determinations in the following manner. Carbon dioxide emissions may be calculated using fuel composition and consumption rate as in Eq.1 or on a fuel basis using fuel energy content and a CO₂ emission factor (Eq.2). A fuel specific emission factor will be calculated as shown in Equations 3 and 4. This

emission factor will then be used with the measured hourly HHV values to calculate CO₂ emissions for the 24 hour period (Eq.2).

Thus, the determination of CO₂ emissions would be measurement based and fuel specific, rather than literature derived. HHV would be determined hourly and CC measured once per day. Each RFG supply stream would be characterized in this manner.

$$\text{(Eq.1)} \text{ECO}_2(\text{massCO}_2/\text{time}) = \text{CC}(\text{massC}/\text{mass fuel}) \times \text{FR}(\text{fuel mass}/\text{time}) \times 44/12$$

Where:

ECO₂ = emission of carbon dioxide

CC = fuel carbon content (measured daily)

FR = fuel flow rate

44/12 = conversion factor from C to CO₂

$$\text{(Eq.2)} \text{ECO}_2 = \text{HHV}(\text{Btu}/\text{fuel mass}) \times \text{FR}(\text{fuel mass}/\text{time}) \times \text{EF}(\text{mass CO}_2/\text{Btu})$$

Where:

HHV = fuel high heating value (measured hourly)

EF = carbon dioxide emission factor

$$\text{(Eq.3)} \quad \text{HHV} \times \text{FR} \times \text{EF} = \text{CC} \times \text{FR}$$

$$\text{(Eq. 4)} \quad \text{EF} = \text{CC}/\text{HHV}$$

ii. Natural gas (NG)

HHV would be determined on a weekly basis and used with a default emission factor to calculate daily CO₂ emissions. Carbon content (CC) would be determined at least once per month. Concurrent HHV and CC determinations will be used to calculate an emission factor (Eq.4). The calculated EF will be reported as a check on calculation accuracy. HHV will either be provided by the NG supplier or measured by the refinery on a weekly basis.

iii. Other fuels

Crude derived "liquefied refinery gases" (LRFGs) may also be used as fuels. For these fuels ARB staff propose that HHV be determined daily and CC weekly. Eq. 4 will be used to calculate a weekly emission factor and daily CO₂ emissions calculated using Eq.2.

Stationary combustion CO₂ emissions from standard fuels such as diesel and gasoline would be calculated using literature derived HHV and EF values (EPA AP-42, API, etc).

b. Methane and Nitrous Oxide (CH₄ and N₂O)

Equipment and fuel specific emission factors would be provided to calculate CH₄ and N₂O stationary combustion emissions from boilers, furnaces, engines and turbines. The factors would be derived from API, AP-42, the Canadian Association of Petroleum Producers (CAPP), IPCC, etc.

6. Cogeneration plants

Reporters will be referred to the cogeneration section of the reporting regulation for emissions calculation and distribution methodologies.

7. Process Emissions

a. Hydrogen production plants (CO₂)

Process emissions, the venting of feedstock derived CO₂, and heater/boiler combustion emissions are important GHG emission sources in a hydrogen plant. Hydrogen plant feedstock may be simple -- for example, when only natural gas is used -- or feedstocks can be complex as is the case when refinery gas, naphtha, and mixtures of these crude derived fuels and natural gas are used. In either case, **Eq.5** would be used to calculate CO₂ process emissions.

(Eq.5)

$$ECO_2 = FSR \times CF \times 44/12$$

Where: FSR = Feedstock Supply Rate

CF = Carbon Fraction in the feedstock.

The CF of all feedstocks (with the exception of natural gas) would be determined on a daily basis. Natural gas composition (CF) would be measured on a weekly basis either by the supplier or the refiner.

The API Compendium provides a second emission calculation methodology based on *hydrogen production rate*. There are two potential sources of error associated with this method which make it problematic. First, this method will result in an overestimation of CO₂ emissions when feed stocks containing hydrogen such as refinery fuel gas are used. In this case,

there is no CO₂ emission associated with the “free” hydrogen contained in the feedstock. An additional source of error, this time resulting in an underestimation of CO₂ emissions, occurs when pressure swing adsorption (PSA – a gas stream purification process) off-gas or tail-gas, which contains hydrogen, is used as a fuel in the reformer furnace. Hydrogen (that may have had attendant CO₂ emissions associated with its generation) is consumed as a fuel and is not accounted for in the measured hydrogen production rate.

b. Catalytic Cracking (CO₂)

Process emissions occur during the continual or intermittent regeneration of catalyst. Accumulated coke must be burned off the catalyst for it to retain its activity. The proposed emissions calculation methodology (**Eq.7**) is based on an API derived method, using process parameters that are routinely monitored for both operational reasons and HAPS emissions permit requirements.

$$\text{(Eq.7)} \quad \text{ECO}_2 = \text{CR} \times \text{CF} \times 44/12$$

Where:

CR = Coke Burn rate (mass/time)

CF = Carbon fraction in coke burned

The coke burn rate is calculated based on an EPA Methodology under Title 40 regulations (40CFR 63.1564), Subpart UUU, National Emission Standards for Hazardous Air Pollutants for Petroleum Refineries: Catalytic Cracking Units, Catalytic Reforming Units, and Sulfur Recovery Units.

$$\text{(EQ.8)} \quad \text{CR} = K_1 Q_r (\% \text{CO}_2 + \% \text{CO}) + K_2 Q_a - K_3 Q_r [(\% \text{CO}/2) + \% \text{CO}_2 + \% \text{O}_2] + K_3 Q_{\text{oxy}} (\% \text{O}_{\text{xy}})$$

Where:

K₁, K₂, K₃ = material balance and conversion factors

Q_r = volumetric flow rate of exhaust gas before addition of air or gas streams

Q_a = volumetric flow rate of air to CC unit regenerator

%CO₂ = CO₂ concentration in regenerator exhaust

%CO = CO concentration in regenerator exhaust

%O₂ = oxygen concentration in regenerator exhaust

Q_{oxy} = volumetric flow rate of O₂ to regenerator

%O_{xy} = O₂ concentration in air stream to regenerator

CF – the carbon fraction in the coke burned would be assumed to be unity (1) unless the refiner supplies this value based on laboratory measurements.

Equation 7 would be used to calculate CO₂ process emissions from fluid catalytic crackers, and flexi-cokers. Other refinery catalytic operations that require periodic rather than continuous catalyst regeneration will use the following methodology (Eq.9) to calculate CO₂ emissions:

(Eq.9)
$$ECO_2 = CRR \times CF \times 44/12$$

Where:

CRR = catalyst regeneration rate (mass/regeneration cycle)

CF = weight fraction of carbon on the catalysts

c. Sulfur Recovery (CO₂)

Stationary combustion emissions resulting from sulfur recovery (heaters, etc) will be characterized by standard stationary combustion methods. However, process emissions resulting from the entrainment and subsequent oxidation of crude derived hydrocarbons sent to refinery sulfur recovery plants are not well characterized. The API Compendium presents no methodology to estimate these process emissions. ARB staff will propose that limited SRU (sulfur recovery unit) tail gas compositional data be used to calculate emissions.

d. Asphalt Production (CO₂)

There are nine California refineries that have asphalt production facilities and at several of these, asphalt is the primary or sole product. The present API methodology is based on very old data (1980) and unsupported assumptions. GHG emissions resulting from combustion of standard fuels such as natural gas, No. 1 and No. 2 fuel oil in heaters (vacuum, hot oil etc.) and boilers would be calculated using **Eq.2**, where HHV is measured weekly by the refiner or by the fuel supplier (natural gas).

Emissions resulting from the combustion of refinery fuel gas will be calculated as outlined in Section 5, Stationary Combustion, non-standard fuels. Uncontrolled emissions resulting from asphalt blowing would be calculated using an EPA default emission factor of 2,555 scf CH₄/Mbbbl. Emissions from flaring would be calculated as described in the

fugitive emissions section below. Emissions from uncontrolled storage tanks would be calculated using the EPA TANKS program.

8. Fugitive Emissions (CH₄)

i. Wastewater treatment

Methane emissions resulting from uncontrolled anaerobic waste water treatment would be calculated using IPCC methodology (IPCC, 2000).

(Eq.) 10

$$E_{CH_4} = Q \times COD \times B \times MCF$$

Where:

Q = volume of wastewater treated

COD = chemical oxygen demand of the wastewater

B = methane generation capacity (IPPC default is 0.25 kg CH₄/kg COD)

MCF = methane conversion factor for the anaerobic decay (IPCC default is 0.5)

ii. Storage Tanks

The applicability of the EPA TANKS model is currently being evaluated for calculation of emissions from uncontrolled storage tanks. A simpler approach using a facility based emissions factor (THC/bbl feedstock) and an assumed CH₄/THC ratio is also under consideration.

iii. Process vents

API methodology will be adopted for the calculation of CH₄ and CO₂ emissions from uncontrolled "cold" process vents.

(Eq. 11)

$$E_x = VR \times F_x \times MW_x / MVC \times VT \times n$$

Where:

E_x = emissions of X (X = CO₂ or CH₄)

VR = vent rate

F_x = molar fraction of X in vent gas stream

MW_x = molecular weight of X

MVC = molar volume conversion

VT = time duration of venting

N = number of venting events per unit time

iv. Flaring

The BAAQMD requires that refiners report daily flaring data. Vent gas flow rate and CH₄, NMHC and SO₂ emissions are reported. SCAQMD also requires flare

emissions reporting. This data may be used with an assumed flare destruction efficiency and NMHC composition to calculate CH₄ and CO₂ flare emissions.

9. Mobile Emissions

ARB staff do not propose to require reporting of mobile source emissions at this time.

10. Indirect Emissions

Refineries would report their purchased electricity (kwh) and heat (BTUs), and the suppliers of that eneRFGy. A requirement to calculate indirect emissions will not be proposed.

11. Verification

As laRFGe and complex sources of GHGs refineries will be required to provide third party verification of emissions reports on an annual basis. Requirements will be specified in the verification section of the regulation.

The Oil and Gas Exploration and Production (E & P) Sector

Background Information

- 1. Who will report?** – Oil and Gas Exploration and Production facilities will be required to report their combustion emissions only, when they exceed the 25,000 MT threshold applicable to general stationary combustion sources.
- 2. What GHGs will be reported?** – At this time only CO₂, CH₄, and N₂O will be reported.
- 3. What emissions sources will be reported?**
 - a. Stationary Combustion

Associated gas (gas recovered during oil production) is used as a fuel in the oil and gas fields to fire heaters and boilers and may be used as a fuel in co-generation plants. The heating value and chemical composition of this gas also varies significantly. For combustion sources in the E&P sector, ARB staff propose to augment the general stationary combustion calculation and reporting methods with the fuel gas sampling schedules and the calculation methods outlined above for the refinery sector.

Co-generation plants under the operational control of E&P entities would report GHG emissions and steam/electricity emission allocations using methods specified in the co-generation section of the regulation.
 - b. Process emissions

E&P facilities will not initially be required to report process emissions. Pending the development and review of appropriate protocols, requirements would be added at a later date.
 - c. Fugitive emissions

E&P facilities will not initially be required to report fugitive emissions. Pending the development and review of appropriate protocols, requirements would be added at a later date.